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**(54) Protective devices**

(57) A glass bottle, especially one carrying carbonated beverages, is coated to avoid hazards on fracture. The coating has inner and outer parts self-bonded to each other. The inner part is a thin, strong, highly stretchable film of a linear

polyurethane having a good recovery after stretching and the outer part is an abrasion-resistant polyurethane. The coating process can be performed at temperatures lower than 100°C and avoids the use of silane sizes. Preferably the bottle is of white flint glass and absorbers and/or tinters are included in the outer part of the coating.

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# SPECIFICATION Protective devices

This invention relates to the protection of glass containers. It is primarily concerned with the protection of glass bottles for carbonated beverages to avoid hazards on fracture.

There are two main approaches to the problem of protecting glass bottles. One approach involves the fitting of plastics sleeves on the bottles, either by shrink fitting or by an adhesive, and the other approach is to apply liquid or powder coatings which are then processed.

The first approach is typically illustrated in the following patent documents: GB 2,023,061 A; GB 1,463,531; GB 1,379,564; GB 1,372,102; GB 1,358,409.

The alternative approach is typically illustrated in the following patent documents: DT 2,744,515; DT 2,745,790; GB 1,545,874; GB 2,021,124 A; GB 1,483,014; GB 1,473,522; EP 0000420; EP 0001148; EP 0001658; EP 0001657; USP 3,415,673; USP 4,163,814.

The first approach can produce results which satisfy rigorous laws concerning safety standards of glass bottles for carbonated beverages. However, the cost tends to be high and, for best results, steps have to be taken to accommodate variations in bottle dimensions where the bottle shape changes (GB 2,023,061 A). It tends also to involve thermal processes at temperatures in excess of 100°C.

The alternative approach has produced only limited commercial success, despite the extensive effort which has been made to use it. Known processes involve temperatures in excess of 100°C, multiple heating steps and the use of pretreatments some of which, such as silane size, are toxic or carcinogenic. Commercial success calls for an approach which aims to satisfy the following criteria:

Low material cost.

Low capital and operating costs for applying the coatings.

Adequate safety during transport, storage and use.

Avoidance of toxicity problems and especially avoidance of the use of silane size pretreatments.

Versatility of the system to cover all aspects of bottle design so that no problem arises with protecting bottles of irregular shapes of having deep contours.

The present invention provides an approach in satisfaction of the above criteria.

A protected glass container according to the present invention, comprises said container having, on its outside, an inner coating of a thin, strong, highly stretchable film of linear polyurethane having a good recovery after stretching and an outer coating of an abrasion resistant moisture or catalytic cured film of polyurethane self-bonded to the inner coating.

The inner coating may be modified by the addition of other compatible polymers such as acrylic resin, and/or ketone resin and/or cellulose derivatives, and/or soluble vinyl chloride copolymers compatible with the polyurethane. The inner coating may be applied from a solution of the polyurethane, and the modifiers, into which bottles are dipped and then dried. Alternatively, the solution may be sprayed onto the bottles and then dried. Drying may be at ambient temperature but may be at higher temperatures. Wash coating may also be used for high throughput.

The dry inner coating is typically about 25 microns thick. On this basis a one litre glass bottle may be given a protective skin of only about 5 to 7 grams. The tensile strength of the skin is typically 30 N/mm<sup>2</sup> with fracture at up to 400% elongation depending on the modifier incorporated. At 300% elongation there is a recovery, typically, of better than 250%. The inner coating above described satisfies all the above stated criteria except that it may lose some of its effectiveness during careless transport, storage, exposure, and use.

In trials with only the inner coating, one litre glass bottles (intended for carbonated beverages) have been exploded by a progressively increasing internal pressure. At fracture, none of the glass in the bottles has become loosely fragmented. The bottles remain intact apart from fracture lines. Fracture pressure had been increased, on average by 25%.

The mechanism by which the coating achieves its objectives is not fully understood but it is thought that a degree of polar surface adhesion of the film to the container is involved although the film does not, of itself, necessarily have any stickiness. This, coupled with the high film strength and with the ability of the film to stretch and recover, appears to accommodate the unexpectedly large deformations which take place when a carbonated beverage bottle shatters.

It is preferred, when used on a necked bottle, that the film is applied up to the top of the neck of the bottle and this probably helps the film perform its intended function.

The outer coating, whilst compensating for any abrasion resistance lacking in the inner coating, also complements the inner coating as there is a self-bonding or cross-linking with the inner coating which not only gives greater rigidity to the inner coating, but also high clarity. It can also provide for moisture-exclusion at the inner coating which prevents moisture interfering adversely with the qualities of the inner coating. The presence of the outer coating also makes it possible to readily and inexpensively include ultra-violet light absorbers to protect the contents of the container, thus making it possible for a bottle to serve a protective function to its contents, whilst remaining as white flint glass. The outer coating may also be tinted, which allows purely decorative or functionally coloured glass

bottles, with or without ultra-violet light absorbers to be manufactured from the cheapest white flint glass. For example, opal effect glass can be simply, safely and inexpensively obtained by additives to the film such as titanium dioxide and ferric oxide. The presence of the outer coating, which provides a carrier for the above additives, avoids the need to put additives in the inner coating. This is meritorious as most additives would act to lower the performance of the inner coating if located there. It also avoids the need to put additives in the glass. This is also meritorious as many glass additives are toxic in their uncompounded form and the additions can increase cost and introduce a risk of lowering moulding efficiency.

A bottle coated in accordance with the invention can handle like glass, look like glass and is not slippery. The invention can be performed at about one-third of the cost of protection by shrink-fitting a plastics sleeve to a bottle. This, arises, in part, as the treatment of the bottle can be carried out at relatively low temperatures (80°C) for a relatively short period (6—10 minutes) with simple (low capital cost) equipment. This is to be compared with a shrink fitted protector, for which a temperature of about 200°C has to be retained for 30 minutes to achieve the required shrinking.

With the present invention, bottles can soon be manually handled and the heat input is low. Further, operation at low temperature of 80°C does not include the risk of altering any annealing effects previously applied to the bottles. There need be no toxicity hazard either in manufacture or use. This is to be compared with known coating methods in which carcinogenic silane sizes are used. No adhesives or adhesive applying steps are required.

An example of the invention will now be described. An inner coating, dipping or spraying lacquer is prepared, having the following formulation:—

	Linear Aliphatic Polyurethane elastomer in isopropanol	P.B.W.	
	(25% solids) — "DESMOLAC" 4125 — by Bayer	45.45	
25	Ketone Resin	4.55	25
	Diacetone Alcohol	22.73	
	Methyl Ethyl Ketone	27.27	
		<hr/> 100.00	

An outer coating, spray lacquer is prepared having the following formulation:

30	Moisture cured aromatic polyurethane in Ethyl Glycol	P.B.W.	30
	Acetate (70% solids) — "DESMOLAC" E 3260 — by Bayer	78.72	
35	10% BASILON OL OL in Ethylene Glycol monoethyl ether — by Bayer	0.23	35
	10% ACRONAL 700 L in Ethylene Glycol monoethyl ether — by Bayer	6.94	
	10% DIBUTYL TIN DILAUATE in Toluene	0.23	
	Ethyl Acetate	11.57	
40	Xylene	2.31	40
		<hr/> 100.00	

Cleaned bottles are immersed in the bath of dipping lacquer, so that the level of the lacquer reaches the top of the necks of the bottles. The bottles are slowly withdrawn, allowed to drain, and then warmed to remove solvents. This produces the inner coat. The bottles are then sprayed with the spray lacquer which is then heated for 8 minutes at 80°C to produce the outer coat and final film. As an alternative to immersion in lacquer the bottles could be spray lacquered.

Whilst the invention has a prime application to non-returnable bottles for carbonated beverages it

can also be applied to phials, flasks, pressurised containers, and other glass containers to enhance strength, to prevent danger from glass splinter, and control the sudden escape of toxic, active flammable or expensive contents from those containers.

One of the merits of the invention as above described is that no pre-treatment of the bottles is required. Bottles can be taken after a conventional "hot-end" and "cold-end" treatment in a bottle-making plant (in which the bottles have traces of fatty acids remaining on their surface) and protected. 5

However it is also proposed that the bottles should be protected after the "hot-end" treatment has been completed in a conventional bottle-making plant. This treatment involves a stannic treatment to strengthen the bottles and to present an active polar surface. As the surface is very active there will be an adsorption of atmospheric fatty acids. These may be removed with a 2% caustic soda wash immediately prior to coating in accordance with the intention so that the coating is applied to a clean active polar surface to give a very high bonding. 10

#### CLAIMS

1. A glass container having on its outside a protection comprising:
  - a) an inner coating of thin, strong, highly stretchable film of linear polyurethane having a good recovery after stretching; and
  - b) an outer coating of an abrasion-resistant moisture or catalytic cured film of polyurethane self-bonded to the inner coating.
2. A container as claimed in claim 1 in which the inner coating is modified by the addition of polymers compatible with the inner coating.
3. A container as claimed in claim 1 or 2 in which the inner coating in the dry state has a thickness of about 25 microns.
4. A container as claimed in claim 1, 2 or 3 in which the inner coating in the dry state has a tensile strength of about 30 N/mm<sup>2</sup> and is capable of accepting an elongation of up to 400% with better than 250% recovery at 300% elongation.
5. A container as claimed in any preceding claim in which the container is of white flint glass and ultra-violet absorbers and/or tinters are carried in the outer coating.
6. A container as claimed in claim 5 in which opalising tinters are carried in the outer coating.
7. A method of making a protected glass bottle as claimed in claim 1 comprising:
  - a) taking the bottle and applying the linear polyurethane elastomer lacquer in a solvent and removing the solvent by warming to form an inner coating in the bottle;
  - b) applying the abrasion-resistant, moisture or catalytic curable polyurethane to said inner coat; and
  - c) heating the curable polyurethane below 100°C to form an outer coating self-bonded to the inner coating.
8. A method as claimed in claim 7 in which the bottle taken in step (a) has traces of fatty acids on its surface.
9. The method of making a protected glass bottle substantially as hereinbefore described with reference to the Example.